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16/04/84.(54) **HIGH TEMPERATURE AND ALKALI-RESISTANT REFRACTORY FIBRE FOR REINFORCING CEMENTITIOUS PRODUCTS AND THOSE REINFORCED PRODUCTS.**(30) Priority: **22.04.83 US 487624**  
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## Description

The present invention relates to the use of fibers composed essentially from silica, alumina and zirconia as a fibrous reinforcement or as a refractory fiber in bulk or blanket form.

To date, most of the work in development of a synthetic inorganic fiber suitable for use in reinforcing cementitious matrices has been performed in the glass area. As used here, the term "glass" refers not only to the vitreous, or non-crystalline, structure of the resultant fiber but, also, to a composition containing one or more fluxing agents, usually alkaline metal oxides. The function of these fluxing agents is to reduce the melting temperature of the batch mix making the composition more fiberizable by such methods as continuous pulling and rotary fiberization (extrusion through holes of a spinner disc). At the same time, however, these fluxing agents generally detract from the chemical inertness of the fiber and reduce the service temperature thereof. In applications requiring both chemical and temperature resistance, (e.g., heat treated cementitious product reinforcement) glass fibers containing alkaline metal oxide fluxes can lose 35% or more of their tensile strength with a corresponding loss of reinforcement effectiveness in the cement matrix. This translates into a lowering of the modulus of rupture of the resulting fiber/cement product (i.e., a direct loss of strength of the reinforced product).

Inorganic fibers consisting essentially of silica, alumina and zirconia are generally known. The article "Refractory Glass Fibers" of GATES and LENT in "Ceramic Bulletin", Vol. 46(2), 1967, page 202 seq. for example discloses compositions of 50%  $\text{SiO}_2$ , 22.5% and 27%  $\text{Al}_2\text{O}_3$  respectively, and 20%  $\text{ZrO}_2$  for the production of "fairly fine long fibers, easy to fiberize" and "long flexible fine fibers" respectively. US-A-3,205,079, relating rather to semicrystalline ceramic bodies than to fibers, discloses among others the composition 55%  $\text{SiO}_2$ , 20%  $\text{Al}_2\text{O}_3$  and 20%  $\text{ZrO}_2$  as being appropriate. A composition of 55%  $\text{SiO}_2$ , 25%  $\text{Al}_2\text{O}_3$  and 20%  $\text{ZrO}_2$  is disclosed in US-A-2,873,197 as being suited for the production of "somewhat coarse fibers" with a high percentage of long fibers. It is noted that above references do not at all mention the problem of chemical resistance in acidic and/or alkaline environments. The same applies to shrinkage properties.

US-A-3,904,424 discloses fibers comprising as principal components  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{MgO}$ . The preferred ranges of named components are 35 to 50%  $\text{SiO}_2$ , 25 to 45%  $\text{Al}_2\text{O}_3$ , 7 to 19%  $\text{ZrO}_2$ , and 3 to 20%  $\text{MgO}$ . The corrosion resistance of the fibers against an alkaline substance is mentioned as being improved by the  $\text{ZrO}_2$  component. In any case, however, the alumina content shall remain below 45%, otherwise a higher temperature would be required for melting the components and the yield of fibers would be reduced.

Zirconia ( $\text{ZrO}_2$ ) has been extensively used as an additive in glass formulations as a means of imparting alkali resistance. See for example US-A-3,859,106, US-A-3,966,481, US-A-4,036,654, and US-A-4,330,628. In addition, zirconia by itself or as a predominant component has been used to formulate refractory compositions with relatively high service temperatures. See for example US-A-2,873,197, US-A-2,919,944, US-A-3,035,929, US-A-3,754,950, US-A-3,793,041, US-A-4,053,321, and US-A-4,119,472. As previously noted, however, the suitability of one ingredient for independent chemical, and temperature resistance does not insure that the composition employing that ingredient will have the required combined chemical and thermal resistance. The combination of simultaneous chemical and thermal attack can produce a highly corrosive environment.

In fact, it was a zirconia containing, ostensibly alkali-resistant glass that proved unsatisfactory for this usage, leading to the present invention. Further, research performed in conjunction with the making of this invention bears this out by showing that not all formulations of the components silica, alumina and zirconia produce the desired chemical and thermal resistances.

It should be noted that the high temperatures (149°C to 593°C corresponding to 300°F to 1100°F) present in curing procedures, accelerate not only the chemical combination of silica and lime and the volatilization of organic fiber and excess water, as intended, but also accelerate other chemical reactions such as the alkaline or acidic attack of reinforcing fibers by the matrix. Therefore, a fiber which may be chemically resistant in an alkaline environment and thermally resistant at 260°C (500°F) outside that environment, will not necessarily be resistant to the combination of conditions.

The refractory fibers for the use according to the claims are formulated by impinging a molten stream upon the surfaces of two rapidly rotating spinners.

In addition, while investigating the realm of silica/alumina/zirconia fibers in search of materials with a special combination of chemically and thermally resistant properties, Applicants discovered a refractory fiber formulation which produces a fiber which is slightly less chemically resistant but significantly more temperature resistant. A number of prior art fibers are rated at 1425°C (2600°F) by their manufacturers. Comparative tests of shrinkage run against these competitive fibers show the fibers of the present invention

to be more thermal-resistant. In addition, this formulation produces a higher melt rate for the same energy input and a greater percentage of recovered fiber per pound of melted batch than conventional alumina/silica refractory melts.

These and other features, advantages and characteristics of the present invention will become better understood after a reading of the detailed description which follows.

#### Brief Description of the Drawing

FIGURE 1 is a triaxial drawing showing the ranges of amounts of silica, alumina and zirconia for the chemically/thermally resistant fibers of the parent invention. The points labeled Z1-Z12 and B1-B7 are the actual experimental melts and P1 and P2 are two production runs;

FIG. 2 is a plot showing the change in the modulus of rupture of fiber/cement samples resulting from 288° C (550° F) heat treatment as a function of silica/alumina ratio of the reinforcing fibers (these data being taken from TABLES IV and V);

FIG. 3 is a plot of strength (MR) versus silica/alumina ratio, the data also coming from TABLES IV and V;

FIG. 4 is a triaxial diagram depicting the claimed formulation of the high temperature refractory fiber composition of the present invention; and

FIG. 5 is an enlargement of a portion of the triaxial diagram of FIG. 4 showing the pertinent area and a number of production runs for this high temperature formulation.

#### Detailed Description of the Preferred Embodiments

Fiber-reinforced cementitious products having a calcium silicate matrix are manufactured for a number of commercial applications requiring thermal resistance and structural strength. One such high density calcium silicate product is marketed under the trademark of MARGINITE by Manville Building Materials Corporation. One use for MARGINITE is the formation of molds for casting molten metals. At one time, these cementitious panels were reinforced with amosite asbestos fibers (see US-A-2,326,516 and US-A-2,326,517). The health problems, both real and imagined, associated with asbestos fibers have led to investigation of other fibers as suitable substitutes as reinforcing fibers for calcium silicate matrices. Suitable formulations, employing up to 40% by weight wollastonite fibers and up to 15% by weight of the panel alkali-resistant glass fibers, were developed in the mid to late 1970's (see US-A-4,111,712 and US-A-4,128,434).

The use of these AR glass fibers which have an average fiber diameter of 12 (or 20) microns necessitated the inclusion of 5% organic fibrous material such as kraft as a processing aid to improve formability of the slurry mix, to slow drainage and to provide green strength. Curing of these panels sometimes requires autoclaving (a steam curing at 186° C  $\pm$  330° F and 6.9 bar  $\pm$  100 psi) to accelerate the silica/calcium hydroxide reaction. In addition, the organic fiber must be burned out by a 288° C (550° F), 432° C (900° F) or 593° C (1100° F) heat treatment. The commercially available alkali-resistant (AR) glass used to reinforce these panels has a formulation of SiO<sub>2</sub> - 01%, ZrO<sub>2</sub>-10.5%, Na<sub>2</sub>O-14.5%, X<sub>2</sub>O-2.5%, CaO-5%, TiO<sub>2</sub>-6.0%. Tests indicated that, following curing, the panels reinforced with AR glass fibers, in some cases, retained less than 70% of their modulus of rupture and/or their specific strength (modulus of rupture over the square of the density, MR/D<sup>2</sup>). Such results indicated a break down of one of the fibrous reinforcement components and further analysis showed that it was the AR glass which failed. A chemically resistant refractory fiber was sought as a substitute for the AR glass.

Initially, four compositions (Z1-Z4) were tried experimentally (see FIG. 1) seeking a fiber with the desired properties. Compositional formulations were targeted, the components added in the desired proportions to a 0.914 m (3 feet) diameter, 0.483 m (19 inch) deep research melter. The compositions were melted electrically with the melt stream exiting through an orifice and impinging on a pair of 0.203 m (8 inch) diameter spinnors rotating at 12,000 r.p.m. This produces fibers which are generally 2-7 microns in diameter, 12.7 mm to 254 mm (0.5 to 10 inches) in length (50.8-76.2 mm  $\pm$  2-3 inch average), and having a varying shot content (35-45%, usually). The fibers were collected and analyzed to substantiate composition and 1 gram samples of these various fibers were boiled in a 0.1 N solution of NaOH for one hour; dried, and weighed to determine % weight loss; the results of these tests are shown in TABLE 1.

TABLE I

Composition (% wt)					
Fiber I.D.	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	% wt loss
Z1	50.0	43.0	6.7	1.16	8.2
Z2	47.3	40.1	12.2	1.17	4.6
Z3	50.1	34.6	15.0	1.45	3.3
Z4	59.1	25.9	14.6	2.28	2.2
Z4	59.1	25.9	14.6	2.28	2.2
2400°F Std RF	53.8	46.0	--	1.19	7.8

In addition, thermal tests were run on these fibers to identify those candidates with the best refractory performance. Bulk fiber was vacuum formed into a felt for each formulation to be tested. Lengths of these fibrous felt samples were precisely measured, placed in a refractory kiln for a specified time and temperature, allowed to cool, and then remeasured. The results are shown in TABLE II along with pour rate (or rate of fiberization), average fiber diameter and shot content. These shrinkages will be lower than for production blanket since the felting has eliminated some of the interstitial shrinkage that will occur in production materials (i.e., these test samples have higher than normal densities).

TABLE II

	2400F Std	2600F Std*	Z1	Z2	Z3	Z4
Pour Rate (Lb/hr)	--	--	1200	550	925	1000
Ave Fiber Dia (Microns)	2.8	3.5	1.9	2.4	3.7	4.7
Shot content (%)	40-45 typ	40-45 typ	48.6	41.5	39.4	40.1
Linear Shrinkage (%)						
a. 2400F-112 Hrs	3.7	--	3.2	2.7	2.2	--
b. 2600F-24 Hrs	--	3.15	4.15	3.5	2.3	4.15
c. 2600F-125 Hrs	--	3.70	4.2	3.5	2.3	4.25
d. 2700F-24 Hrs	--	6.1	7.3	6.8	3.2	9.2
e. 2700F-125 Hrs	--	10.1	3.9	7.6	3.7	--

\*This fiber composition is disclosed and claimed in US-A-3,449,137 and has a formulation of 40-60% silica, 35-55% alumina, and 1-8% chromia. The specific fibers used in these tests were 43.5% silica, 53% alumina and 1.5% chromia.

The results of these tests indicated that Z3 had the best thermal performance and acceptable alkali resistance while Z4 had the best alkali resistance with acceptable (disregarding the 1482° C  $\approx$  2700° F reading) thermal performance. It was determined that two separate families of fibers should be pursued, one seeking to optimize thermal performance based on the Z3 formulation and the other seeking to optimize the alkali resistance in more moderate temperature environments (<1093° C  $\approx$  2000F), based on the Z4 formulation. It was believed that increasing alumina and/or zirconia in the Z3 formulation would improve refractoriness and that increasing silica and/or zirconia in the Z4 formulation would enhance alkali resistance.

Accordingly, a family of fibers (B1-B7) based on the Z3 formulation was produced using the 0.914 m (3 feet) research melter in accordance with the procedures outlined above. These formulations are depicted on the triaxial diagram in FIG. 1. These fibers were then subjected to a plurality of temperatures for various

periods of time in the refractory kiln to determine refractoriness. The results of these tests and the formulations of the B1-B7 fibers appear in TABLE III.

TABLE III

	Z3	B1	B2	B3	B4	B5	B6	B7
Components (wt %)								
SiO <sub>2</sub>	50.1	31.3	29.9	30.3	35.3	27.6	24.1	27.6
Al <sub>2</sub> O <sub>3</sub>	34.6	53.2	45.5	41.3	48.2	53.1	55.0	58.4
ZrO <sub>2</sub>	15.0	15.3	15.2	20.2	16.2	19.1	10.6	13.7
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	1.45	.59	.65	.93	.73	.52	.62	.47
SiO <sub>2</sub> /ZrO <sub>2</sub>	3.34	2.046	2.559	1.806	2.179	1.445	3.217	2.015
Temp/Time                      Linear Shrinkage (%)								
2200F/24 Hr	1.94	2.72	--	--	2.92	3.01	3.52	2.93
2400F/24 Hr	2.47	2.83	--	--	2.63	2.80	4.50	2.20
2600F/40 Hr	2.94	2.94	--	--	2.90	3.54	4.69	3.23
2700F/24 Hr	3.42	4.07	5.94	6.34	4.79	4.22	3.68	3.05
2700F/100 Hr	4.7	5.1	10.4	9.6	7.1	4.8	6.8	3.9
2700F/260 Hr	5.4	6.0	14.5	12.7	9.3	5.2	8.8	4.9
2800F/24 Hr	+50.0	13.0	19.4	19.6	20.0	14.2	19.3	10.5

Even though these tests succeeded in producing a fiber with approximately 10% shrinkage at 1538° C (2800° F) as opposed to 50+% for Z3, these tests did not result in the definition of a commercially viable fiber. First, all of these high alumina formulations (B1-B7) were significantly more difficult to fiberize than Z3. Secondly, these fibers all showed a low degree of thermal stability at temperatures above 1093° C (2000° F). Fibers B1, B5 and B7 devitrified and lost their fibrous nature between 1093° C (2000° F) and 1316° C (2400° F). Such behavior would preclude their use as an insulation, as a high-temperature reinforcing fiber or for any other industrial use. The degradation of fibers B2, B3, B4 and B6 was not as great; however, these fibers had linear shrinkage from 8 to 15% after 260 hours of exposure to 1482° C (2700° F). Such high shrinkages would make these fibers unacceptable, as well, for any commercial application. Note, also, each of these fibers (B2, B3, B4 and B6) failed to produce samples of less than 5.0% linear shrinkage for 100 hours of exposure to 1482° C (2700° F). In order to be rated at a particular temperature, a fiber sample of this type (i.e., felted) should exhibit no more than 5% linear shrinkage after 100 hours of heat soaking. This insures that a particular fiber will not undergo unacceptable levels of shrinkage (i.e., exceeding 12%) when cycled up to its service temperature repeatedly throughout its service life. When the fiber samples are collected in a normal production run and needled into a blanket, rather than being pressed into a felt, the shrinkages seen in this type of test will be more akin to the maximum shrinkages desired during use.

Production runs of various formulation chemistries were made to determine which formulations 1) fiberized well; 2) made fibers with acceptable levels of shrinkage; and 3) could achieve production results comparable to those achieved in the test melter. It was during these production runs that the advantages of these zirconia formulations became apparent. In a stabilized melter of the same configuration used formerly for silica/alumina melts (both top- and bottom-ontry electrode), the zirconia formulation produced higher pour rates for the same energy input and significantly better percentages of recovered fiber per pound of melted batch (i.e., lower shot content and less rejected blanket).

Samples of these various blanket formulations were analyzed for chemistry and tested for shrinkage as before. The amount of linear shrinkage is a time/temperature phenomenon. Accordingly, although this fiber will probably be targeted for usage in the 1400 to 1455° C (2550 to 2650° F) range, the samples were

inserted in a kiln at 1482° C (2700° F) for four hours to 1) accelerate the tests thereby reducing the time required and 2) to insure that the blanket could withstand limited exposure to peak temperatures above those recommended for usage without catastrophic failure. The results of these tests appear in TABLE IIIA.

TABLE IIIA

% By Weight					
Sample No.	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	SiO <sub>2</sub> /ZrO <sub>2</sub> Ratio	% Linear Shrinkage
1	53.1	45.8	0.4	132.75	15.6
2	51.9	42.5	4.6	11.282	14.6
3	50.0	44.3	5.3	9.434	14.9
4	51.7	42.1	5.4	9.57	13.3
5	49.0	38.9	11.2	4.375	12.1
6	48.0	38.2	13.2	3.636	9.2
7	49.2	36.4	13.8	3.565	8.2
8	54.7	30.3	14.1	3.879	12.9
9	49.4	35.0	14.5	3.407	11.3
10	50.2	34.1	14.7	3.415	9.7
11	51.9	32.9	14.7	3.531	9.1
12	49.7	34.7	15.0	3.313	8.8
13	49.7	34.3	15.0	3.313	8.2
14	47.6	37.3	15.2	3.132	10.9
15	49.3	34.6	15.3	3.222	9.7
16	46.0	37.3	15.3	3.007	9.0
17	46.4	37.2	15.4	3.013	8.1
18	46.2	37.0	15.5	2.98	6.8
19	46.2	31.3	15.6	2.961	7.2
20	50.1	32.0	17.4	2.879	7.8
21	49.3	32.4	17.4	2.833	7.4
22	47.2	34.4	17.5	2.697	8.6
23	47.4	33.9	17.6	2.693	6.0
24	47.4	34.2	17.7	2.678	7.2
25	48.0	33.2	17.8	2.697	7.3
28	47.7	33.4	17.8	2.680	7.2

For these tests, an acceptable level of shrinkage is defined as 11.5%. While this may seem like an inordinately high level of shrinkage, it should be remembered that the amount of shrinkage has been intentionally aggravated by exposing these samples to a temperature (1482° C  $\approx$  2700° F) exceeding its recommended service temperature (1399-1454° C  $\approx$  2550-2650° F). Secondly, much of the blanket made using this formulation will find its way into insulation modules of the type described in US-A- 4,001,996. In such a modular configuration, the blanket will undergo less shrinkage since only a small portion of its surface is exposed to the internal furnace temperatures. Further, a major portion of any gap which might form as a result of such shrinkage will be filled as the compressed modules expand.

From TABLE IIIA, it appears that the formulations producing fiber with acceptable shrinkage level have the following compositions: SiO<sub>2</sub> ranging from 48.0 to 52%, Al<sub>2</sub>O<sub>3</sub> ranging from 32 to 38% and ZrO<sub>2</sub> ranging from 13 to 18% (all percentages are percent by weight). As a further restriction on this family of formulations, the silica to zirconia ratio appears to be significant and should not exceed 3.8. From TABLE III, the SiO<sub>2</sub>/ZrO<sub>2</sub> ratio for the defined zirconia range (13-18%) has a minimum of 2.6. Within this family, a more preferred formulation (based on shrinkages) is SiO<sub>2</sub> from 46.4 to 50.1%, Al<sub>2</sub>O<sub>3</sub> from 32 to 37.3%, ZrO<sub>2</sub> from 15 to 18%, and a SiO<sub>2</sub> to ZrO<sub>2</sub> ratio of between 2.6 and 3.32.

The results from TABLE IIIA are depicted graphically in FIG. 4 with the family of formulations shown in solid line. FIG. 5 is an enlargement of a portion of the triaxial diagram of FIG. 4 (shown in dotted line) to enable the plotted formulations to be seen more clearly. Even in the enlarged view of FIG. 5, two points (samples 13 and 19) were too close to other formulations to be plotted as distinctly separate points.

Both the fiber in bulk form and in blanket are usable to 1426° C (2600° F). In order to compare this fiber to other fiber rated to 1426° C (2600° F), blanket samples of the disclosed fiber (having a formulation of 40.7% SiO<sub>2</sub>, 34.7% Al<sub>2</sub>O<sub>3</sub> and 15.0% ZrO<sub>2</sub>), were tested for shrinkage in side-by-side furnace tests to 1) a commercially available refractory fiber blanket having the formulation Al<sub>2</sub>O<sub>3</sub>-54%, SiO<sub>2</sub>-46%; b) a commercially available refractory fiber blanket which has undergone a heat treatment (i.e., has been preshrunk) and has a composition of 51% alumina, 49% silica; and c) a commercially available refractory fiber blanket with the formulation of SiO<sub>2</sub>-51.6%, Al<sub>2</sub>O<sub>3</sub>-47.7%, the blanket having subsequently received a surface treatment of 1/2% chromium oxide.

Strips of these four blanket samples were tested for shrinkage in a manner performed in the previous tests. Measured lengths of blanket were placed in a kiln at 1400° C (2550° F) and remeasured after each of 25, 50 and 75 hours percent shrinkage was computed by dividing the change in length by the original length and multiplying by 100. Due to the relatively small amount of shrinkage change between the 50 and 75 hour measurements, subsequent tests run at 1426° C (2600° F) and 1482° C (2700° F) were run only to 50 hours. The results of these tests appear in TABLE IIIB.

TABLE IIIB

% Linear Shrinkage							
Sample	25 Hr	50 Hr	75 Hr	25 Hr	50 Hr	25 Hr	50 Hr
Disclosed fiber	3.0	3.1	3.1	3.2	3.2	5.7	5.7
54/46 formulation	4.2	4.9	5.0	5.0	5.7	4.8	5.7
51/49 formulation	3.4	3.6	3.6	4.6	4.6	6.7	6.9
Chrome treated	3.6	3.9	4.0	4.1	4.3	10.5	11.2

These tests show the superiority of the disclosed fiber to these three other commercially available fibers. When taken in conjunction with the difficulties of fiberizing a high alumina composition, problems associated with chromia treatment, the aforesaid improvements in pour rate and fiber recovery rate as against other silica/alumina melts, the high temperature formulation of the present invention is clearly superior to other known refractory fiber compositions.



A second family of fibers based on the Z4 composition was formulated (Z5-Z12) and each was fiberized as before. These compositional formulations are shown in TABLE IV along with the Z3 and Z4 formulations, for comparison.

TABLE IV

Fiber Ingredient (% wt)	23	24	25	26	27*	28	29	210**	211	212
SiO <sub>2</sub>	50.1	59.1	57.0	60.4	52.6	67.0	49.7	50.0	73.3	66.4
Al <sub>2</sub> O <sub>3</sub>	34.6	25.9	31.5	18.7	21.3	23.5	22.4	21.9	21.1	15.1
ZrO <sub>2</sub>	15.0	14.6	11.1	20.4	18.1	9.1	27.1	27.4	5.1	18.1
CaO	--	--	--	--	7.75	--	--	--	--	--
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	1.45	2.3	1.8	3.2	2.5	2.9	2.2	2.3	3.5	4.4

\*For inclusion in the triaxial diagram of FIG. 1, these percentages have been recalculated based on a total of 92 parts (SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>+ZrO<sub>2</sub>).

\*\*It was originally intended that 29 and 210 would have significantly different formulations. Because of the similarity of the two compositions, no further tests were performed using 210.

It was decided to test each of these fibers in a calcium silicate matrix of the type in which they were designed to be used. Initial experiments indicated that these smaller diameter fibers (2-7 microns) might not have the forming and filtering problems associated with the AR glass (12 micron diameter) and, if these fibers could provide the fiber/cement product with sufficient green strength, the amount of the kraft added could be significantly reduced or possibly eliminated. This had the possibility of reducing or eliminating the previously required heat treatment and its related cost.

With that in mind, 76.2 mm x 203.2 mm x 25.4 mm (3" x 8" x 1") laboratory samples of a MARINITE-like product using the various fibers Z3-Z12 and B3 were press molded from a slurry with a water to solids ratio 4.3 to 1 and the following composition (percentages are by weight): Kraft - 1.9% (reduced by over 60% from the standard 5%), alkali-resistant refractory fiber (ARRF) - 5.6%, hydrated lime - 24.8%, Celite 392 (a silicate, diatomaceous earth) - 24.8% and Wollastonite - 43.3%. The calcia and silica are provided in equal amounts in order that the two components may react to form the crystalline form, tobermorite. Prior to inclusion, the fibers were placed in a Waring blender for about 60 seconds to reduce the average fiber length to the 3.175 to 12.7 mm (1/8 to 1/2") range. The samples were allowed to gel in the mold for 8 minutes at 88° C (190° F) and pressed to their final 25.4 mm (1") thickness using 137.9 bar (2000 psi). The samples were then autoclaved at 165° C (330° F) and 6.9 bar (100 psi) steam pressure for 20 hours followed by drying at 110° C (230° F).

The samples were then placed in an Instron testing machine and load applied thereto until failure. The testing machine measures deflection and load magnitude. These data are then used with the sample size and thickness to compute flexural modulus of rupture. The flexural modulus of rupture (MR), density (D) and specific strength (MR/D<sup>2</sup>) of these samples were compared to those of similar samples which were

additionally heat treated at 288 °C (550 °F). The values and the percent weight loss and percent change in MR and MR/D<sup>2</sup> are shown in TABLE V.

TABLE V

Reinforcement	Oven Dried			Heat Treated (550°F)			Comparison			
	D (lb/ft <sup>3</sup> )	MR (psi)	MR/D <sup>2</sup>	D	MR	MR/D <sup>2</sup>	% wt. loss	% chg MR	% chg MR/D <sup>2</sup>	
Fiber										
Z3	49.0	909	.38	47.0	810	.37	4.2	-11	-3	
Z4	45.9	940	.47	45.9	1002	.48	1.7	+1	+2	
Z5	52.0	1033	.38	50.9	1084	.42	5.7	+5	+11	
Z6	47.1	802	.41	45.7	874	.42	4.4	-3	+2	
Z7	46.2	927	.43	45.4	899	.44	4.3	-3	+2	
Z8	56.5	1212	.39	54.3	1212	.41	7.3	-2	+5	
Z9	50.1	855	.33	48.9	861	.36	7.0	+3	+9	
Z11	53.5	910	.32	52.2	939	.34	6.1	+3	+6	
Z12	52.7	858	.31	50.0	762	.30	5.1	-11	-3	
B3	46.7	937	.43	46.5	767	.35	3.6	-18	-19	
AR Glass	45.2	965	.47	42.9	717	.39	9.6	-26	-19	

Interpreting TABLE V results in view of the fiber compositions shown in TABLE IV, all samples which were reinforced by fibers with a silica/alumina ratio between 1.8 and 4.0 (Z4-Z11) showed a change in modulus of rupture of  $\pm 5\%$ . Such variation is within experimental error (i.e., strength variations within the

sample following organic burnout, accuracy of the test equipment, etc.) In addition, each of these same samples exhibited an increase in specific strength (MR/D<sup>2</sup>). These results suggest that there has been no loss of strength by the reinforcement fiber as a result of the combined alkali and thermal attack. The samples using fibers with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios outside the 1.8 to 4.0 range, on the otherhand, (Z3, Z12, B3 and AR glass) experienced MR losses exceeding 10% and also had losses of specific strength following 288° C (550° F) heat treatment. These results suggest that the combined alkali and thermal attack have degraded these fibers and impaired their ability to reinforce the cement matrix. These results are graphically depicted in FIG. 2.

The combined results of TABLE IV and V are depicted in a different manner in FIG. 3. The strength (MR) values are plotted versus ascending silica/alumina ratio with the fiber designation and zirconia content also being shown. This graphically depicts that the percent change in MR for heat treated samples is small versus MR for oven dried samples for those fibers of the present invention (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> between 1.9 and 4.0). It is interesting to note that if the samples having fibers of the present invention were to be plotted in order of ascending zirconia content, strength would uniformly decrease from a maximum at 9.1% zirconia to a minimum at 27.1% zirconia. This limited data suggest there may be an optimum zirconia value of 9% (or between 5 and 9%) for producing a reinforcing fiber. Additional zirconia does not appear to benefit alkali resistance at temperature.

To verify these tests, two production fibers were manufactured in a full sized melter, P1 based on Z3 and P2 based on Z4. The compositions were varied slightly from the Z3 and Z4 formulations to determine what effect these compositional changes might have on fiber characteristics. 3,243.2 kg (7150 pounds) of P1 fiber was produced having a planned formulation of 49% SiO<sub>2</sub>, 37% Al<sub>2</sub>O<sub>3</sub> and 14% ZrO<sub>2</sub>. Approximately 39,485.2 kg (87,050 pounds) of P2 fiber was produced having a planned formulation of 62% SiO<sub>2</sub>, 24% Al<sub>2</sub>O<sub>3</sub> and 14% ZrO<sub>2</sub>. Both melts were made in a top-entry electrode, open-topped melter generally of the type described in U.S. patent 3,883,308. P1 has a liquidus temperature of 1760° C (3200° F) and was fiberized at an average melt rate of 491.2 kg/h (1083 lb/hr) using 800 kw of power producing a stream temperature of 1843° C (3350° F). While the actual fiber composition for P1 varied considerably from the planned formulation, analysis showed some of the fiber produced to have the following composition: 49.2% SiO<sub>2</sub>, 36.5% Al<sub>2</sub>O<sub>3</sub> and 13.6% ZrO<sub>2</sub>. This formulation compares favorably with the original Z3 fiber having a 50.1/34.6/15.0 composition. These two formulations showed only .9/1.9/1.4% deviation from each other. Yet, the linear shrinkage for the P1 samples varied from 7.0 to 9.6 following only 24 hours exposure to 1482° C (2700° F). This suggests that the Z3 formulation must be controlled quite closely (± 1%) in order to produce an acceptable 1482° C (2700° F) fiber.

P2 has a liquidus temperature of 1693° C (3080° F) and was fiberized at an average melt rate of 483.5 kg/h (1066 lb/hr) also using 800 kw of power producing a stream temperature from 1793° C (3260° F) and 1827° C (3320° F). Fiber analysis indicated actual formulation was generally within + 2% of the targeted formulation for the majority of the run. Weighted samples of this and the standard 1318° C (2400° F) and 1427° C (2600° F) fibers were placed in various acid and alkaline solutions for 4 hours at 90°C, dried and then weighed, to determine comparative chemical resistance. TABLE VI sets forth the results of these tests.

TABLE VI

% Weight Loss			
Solution	Std. 2400°F	Std. 2600°F	P2 ARRF
0.02 N H <sub>2</sub> SO <sub>4</sub>	5.0	1.4	0.8
1.0 N H <sub>2</sub> SO <sub>4</sub>	1.5	0.5	0.4
0.02 N HCl	1.5	0.6	0.5
1.0 N HCl	5.7	1.3	0.5
0.02 N HNO <sub>3</sub>	1.6	0.5	0.5
0.02 N HF	6.0	8.2	0.4
0.02 N H <sub>3</sub> PO <sub>4</sub>	0.7	0.1	0.3
1.0 N H <sub>3</sub> PO <sub>4</sub>	6.5	1.3	0.1
0.1 N NaOH	14.7	-	2.4

The data from TABLE VI indicates that the P2 fibers (hereafter ARRF) are considerably more chemically inert than other refractory fibers. To further substantiate that these fibers were suitable for reinforcing MARINITE products, a portion of the 39,462.5 kg (87,000 pounds) was shipped to the fiber/cement panel manufacturing plant to, again, verify the results of the small scale tests in full scale production.

5 These fibers were intermixed in a hydropulper in a formulation having the following composition: 2.8% bentonite, 2.8% Kraft, 28.4% CELITE 392, 28.4% lime, 31.9% wollastonite, and 5.7% ARRF. The ARRF fibers were added last to minimize degradation (breakage due to brittleness) during mixing. The slurry was then fed to a mold and pressed to thickness of 25.4 mm (1") and 50.8 mm (2") in 1.22 m (4') by 2.44 m (8') panels using 241.4 bar (3500 psi). Following oven drying and autoclaving, some of the panels were heat  
10 treated at 288°C (550°F).

While some problems have been encountered with surface and edge cracking, those problems have been determined to relate to excess moisture retention (6-9% by weight as opposed to the normal 2-3%) and not to the use of ARRF fibers. These problems are being resolved by modifying slurry composition (reduce or eliminate bentonite and Kraft and increase wollastonite to 45%) and by processing modifications.  
15 ARRF has shown itself to be a suitable reinforcing fiber for calcium silicate cementitious products of the MARINITE variety. Additional MARINITE tests utilizing 402°C (900°F) and 593°C (1100°F) heat treatments further dramatically demonstrate ARRF's superiority to AR glass.

ARRF has also proven useful in reinforcing other calcium silicate products of the type sold by Johns-Manville Corporation under the trademarks AEGEAN, CHEMSTONE, COLORLITH, EBONY, MAGNA and  
20 TRANSITE. While these products have varying compositions they all have the same basic formulation including a calcium component (cement or lime), a silica component (which may be diatomaceous earth), and a fibrous component (up to 45% by weight Wollastonite with or without kraft). In each case, the addition of ARRF permits a significant reduction in the amount of organic (Kraft) fiber used and presents the possibility that the Kraft and/or the heat treatment the use of large amounts of organic fiber requires, may be eliminated. Further the inclusion of ARRF in these panels significantly improves their weatherability and  
25 enables them to be used for exterior applications. ARRF is also suitable for reinforcing mineral panels requiring only normal cure (room temperature for 21 days). However, care must be taken in this and all applications to preserve the fibers by minimizing the time they must be mixed in the pulper. ARRF should be among the last ingredients to be added.

30 In formulating these various compositions, it is necessary to use ingredients that have a certain degree of purity. This ARRF composition is not as sensitive to impurities as some glass or refractory batches. The formulations of the present invention can tolerate up to 0.5% of most of the more common impurities including alkali metal oxides. Further as the Z7 composition indicates, the ARRF fibers can tolerate up to 10% alkaline earth metal oxides (CaO and MgO) without detrimentally affecting the high temperature alkali  
35 resistance of the fiber. Of course, the inclusion of CaO or MgO in the Z3 formulation would adversely affect the high temperature performance of that fiber. In fact, in order to insure the high temperature performance of this fiber, impurity levels, particularly for alkali metal oxides and alkaline earth oxides, must be kept at or below levels normally desired for high temperature silica-alumina refractory fibers.

Suitable batch ingredients include Zircon sand (-325 mesh flour) available from Continental Minerals as  
40 582 W.S. Zircon, a 200 mesh ground silica available from Wedron Silica Company, and any number of 200 mesh aluminas, for example, normal soda grade alumina such as C1 grade available from Kaiser Corporation or A-1 grade available from Aluminum Company of America.

With regard to fiber diameter, it has been previously mentioned that these ARRF fibers generally fall in the 2-7 micron range. For normal fiberizing conditions (i.e., melt stream 66-121°C (150-250°F) above  
45 liquidus, pour rate 453.6-480.9 kg/h (1000-1100 pounds/hour), spinner rotation rate 12,000 r.p.m.) the average fiber diameter generally falls in the 2-4 micron range. Because chemical attack is a surface phenomenon, it would be preferable to have a larger diameter fiber in order to present less surface area per pound of reinforcement fiber. However, as was seen with the AR glass, a very large fiber causes drainage and forming problems necessitating the addition of organic fibers with additional resultant problems. From  
50 the tests that have been run, the optimum fiber diameter appears to be in the 5-8 micron range. Fiber diameter can be increased by changing one or more of the process variable as follows: reduce the stream temperature 10-38°C (50-100°F), reduce the pull rate 10-20%, and/or slow the spinner to the range of 8000-10000 r.p.m. Since even the smaller diameter fibers out performed the AR glass it is replacing, this fiber diameter optimization can only serve to further enhance ARRF's performance.

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Various charges, alternatives and modifications will be apparent following a reading of the foregoing specification. For example, it is contemplated that the addition of up to 2.5% chromia to the Z3 formulation may be beneficial in improving refractoriness. Also, although only one fiberization technique has been discussed, this refractory fiber may be formed using any other commercial technique, such as blowing, for example.

#### Claims

1. The use of fibers of a composition being essentially free of alkali metal oxides and comprising, by weight percent:-

SiO <sub>2</sub>	45 - 76%
Al <sub>2</sub> O <sub>3</sub>	12 - 32%
ZrO <sub>2</sub>	5 - 30%

and having a silica to alumina ratio in the range from 1.8 to 4.0, as an essentially chemically inert synthetic inorganic fibrous reinforcement capable of withstanding temperatures exceeding 500° F (260° C) with virtually no loss of tensile strength and being resistant to alkaline or acidic environments at such temperatures.

2. The use of fibers according to claim 1 wherein the compositional ranges are, by weight percent, from 49.7 to 73.3% for silica, from 18.7 to 31.5% for alumina, and from 5.1 to 27.4% for zirconia.
3. The use of fibers according to claim 1 wherein the composition includes up to 10% by weight alkaline earth metal oxides.
4. The use of fibers according to claim 1 wherein the silica to alumina ratio lies in the range from 1.8 to 3.5.
5. The use of fibers of a composition consisting of in percent by weight:-

SiO <sub>2</sub>	46 - 52%
Al <sub>2</sub> O <sub>3</sub>	32 - 38%
ZrO <sub>2</sub>	13 - 18%

and having a silica to zirconia ratio in the range of from 2.6 to 3.8 as a high temperature refractory in bulk or blanket form exhibiting superior shrinkage resistance of less than 11.5% when subjected to temperatures up to 2,700° F (1,482° C) for about four hours.

6. The use of fibers according to claim 5 wherein the compositional ranges are in percent by weight from 46.4 to 50.1% for silica, from 32.0 to 37.3% for alumina, and from 15.0 to 18.0% for zirconia and wherein the silica to zirconia ratio is between 2.6 and 3.32.

#### Revendications

1. Utilisation de fibres d'une composition sensiblement exempte d'oxydes de métaux alcalins comprenant, en pourcentages pondéraux :

SiO <sub>2</sub>	45 - 76%
Al <sub>2</sub> O <sub>3</sub>	12 - 32%
ZrO <sub>2</sub>	5 - 30%

et présentant un rapport de la silice à l'alumine dans l'intervalle de 1,8 à 4,0, comme renforcement fibreux inorganique synthétique en substance chimiquement inerte capable de résister à des températures excédant 500° F (260° C) virtuellement sans perte de la résistance à la traction et résistant aux

milieux alcalins ou acides à ces températures.

2. Utilisation de fibres suivant la revendication 1, dans laquelle les intervalles de composition sont, en pourcentages pondéraux, de 49,7 à 73,3% pour la silice, de 18,7 à 31,5% pour l'alumine et de 5,1 à 27,4% pour la zircone.
3. Utilisation de fibres suivant la revendication 1, dans laquelle la composition comprend jusqu'à 10% en poids d'oxydes de métaux alcalino-terreux.
4. Utilisation de fibres suivant la revendication 1, dans laquelle le rapport de la silice à l'alumine se situe dans l'intervalle de 1,8 à 3,5.
5. Utilisation de fibres d'une composition consistant, en pourcentages pondéraux, en :

SiO <sub>2</sub>	46 - 52%
Al <sub>2</sub> O <sub>3</sub>	32 - 38%
ZrO <sub>2</sub>	13 - 18%

- et présentant un rapport de la silice à l'alumine de l'intervalle de 2,6 à 3,8 comme réfractaire pour haute température en masse ou en nappe manifestant une résistance supérieure au retrait, qui est inférieure à 11,5% lors d'une exposition à des températures s'élevant jusqu'à 2700 °F (1482 °C) pendant environ 4 heures.
6. Utilisation de fibres suivant la revendication 5, dans laquelle les intervalles de composition sont, en pourcentages pondéraux, de 46,4 à 50,1% pour la silice, de 32,0 à 37,3% pour l'alumine et de 15,0 à 18,0% pour la zircone, le rapport de la silice à la zircone se situant entre 2,6 et 3,32.

#### Patentansprüche

1. Verwendung von Fasern mit einer Zusammensetzung, die im wesentlichen frei von alkalischen Metalloxiden ist und folgendes in Gewichtsprozenten umfaßt:

SiO <sub>2</sub>	45-76%
Al <sub>2</sub> O <sub>3</sub>	12-32%
ZrO <sub>2</sub>	5-30%

und ferner ein Verhältnis von Silikamasse zu Aluminiumoxid im Bereich von 1,8 bis 4,0 aufweist, als im wesentlichen chemisch inerte anorganische Synthetikfaserverstärkung, die 500 °F (260 °C) übersteigende Temperaturen praktisch ohne Verlust an Zugfestigkeit aushalten kann und sowohl in basischen als auch in sauren Umgebungen bei solchen Temperaturen resistent ist.

2. Verwendung von Fasern nach Anspruch 1, deren Bestandteile sich anteilmäßig vorzugsweise in Bereichen von 49,7 bis 73,3% für Silikamasse, von 18,7 - 31,5% für Aluminiumoxid und von 5,1 - 27,4% für Zirkoniumoxid bewegen.
3. Verwendung von Fasern nach Anspruch 1, mit bis zu 10 Gew.% an alkalischen Erdmetalloxiden.
4. Verwendung von Fasern nach Anspruch 1, bei der das bevorzugte Verhältnis von Silikamasse zu Aluminiumoxid im Bereich von 1,8 - 3,5 liegt.
5. Verwendung von Fasern mit einer Zusammensetzung, die folgendes in Gewichtsprozenten umfaßt:

SiO <sub>2</sub>	46-52%
Al <sub>2</sub> O <sub>3</sub>	32-38%
ZrO <sub>2</sub>	13-18%

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und ferner ein Verhältnis von Silikamasse zu Zirkoniumoxid im Bereich von 2,6 bis 3,8 aufweist, als bei hohen Temperaturen feuerfestes Material in Form einer Masse oder eines Rohlings, der unter Einwirkung von Temperaturen bis zu 2700 °F (1482 °C) während einer Dauer von etwa 4 Stunden eine höchste Schrumpffestigkeit von weniger als 11,5% aufweist.

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6. Verwendung von Fasern nach Anspruch 5, deren Bestandteile sich in Gewichtsprozent vorzugsweise in Bereichen von 46,4 bis 50,1 für Silikamasse, von 32,0 - 37,3% für Aluminiumoxid und von 15,0 - 18,0 für Zirkoniumoxid bewegen, wobei das Verhältnis von Silikamasse zu Zirkoniumoxid im Bereich von 2,6 - 3,32 liegt.

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